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(54) COATING COMPOSITION HAVING HIGH REFRACTIVE INDEX

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an inexpensive coating composition having a high refractive index, excellent physical properties such as hardness, resistance to scratching, adhesivity, etc., and improved productivity.

SOLUTION: This coating composition comprises a metal alkoxide of general formula (1)  $M(OR)_n$  (M is any one metal of Ti, Ta, Zr, In and Zn; R is an alkyl group; n is an oxidation number of metal) and its hydrolyzate and an organosilicon compound of general formula (2)  $R'_xSi(OR)_y$  (R is an alkyl group; R' is a functional group containing a polymerizable unsaturated bond such as vinyl group, acryloyl group, methacryloyl group or the like at the end; y is an oxidation number of metal; x is a substitution number of  $0 < x < y$ ) and its hydrolyzate as main components.

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**CLAIMS**  
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[Claim(s)]

[Claim 1] The following general formula (1)

The metal alkoxide which can be expressed with  $M(OR)_n$  (an alkyl group and n are [ M ] the metaled oxidation number for any one sort of metals of Ti, Ta, Zr, In, and Zn, and R) and its hydrolyzate, and the following general formula (2)

R'<sub>x</sub> High refractive-index coating constituent which uses as a principal component the organic silicon compound which can express with  $Si(OR)_y$  (the metaled oxidation

number and x are the number of permutations of  $0 < x < y$  for the functional group and y to which an alkyl group and R' have the unsaturated bond in which polymerizations, such as a vinyl group, an acryloyl radical, and a methacryloyl radical, are possible at the end in R), and its hydrolyzate.

[Claim 2] The high refractive-index coating constituent according to claim 1 characterized by coming further to contain the isocyanate compound which has at least two or more isocyanate radicals in a molecule in said coating constituent.

[Claim 3] The high refractive-index coating constituent according to claim 2 characterized by for said ISON cyanate compound being the denaturation object of hexamethylene di-isocyanate (HDI), and mean molecular weights being 500-3000.

[Claim 4] Which the high refractive-index coating constituent according to claim 1 to 3 with which OH \*\* has 15-400, and average molecular weight is further characterized by coming to contain the polyol resin of 3000-30000 into said coating constituent.

[Claim 5] Which the high refractive-index coating constituent according to claim 1 to 4 characterized by coming further to contain the high refraction ultrafine particle chosen from crystalline titanium oxide of 1-50nm of mean diameters, a zirconium dioxide, a zinc oxide, and indium oxide in said coating constituent.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] About a high refractive-index coating constituent, in more detail, coating of this invention is carried out to transperance base materials, such as glass and plastics, etc., and it relates to the high refractive-index coating constituent which can form optical multilayers, such as an antireflection film, permselective membrane, or absorption film.

[0002]

[Description of the Prior Art] Conventionally, the approach of forming inorganic oxide thin films, such as titanium oxide and silicon oxide, in base materials, such as glass and plastics, by dry coating, such as vacuum deposition or a spatter, and forming the optical multilayers by optical interference of an antireflection film etc. is learned. However, in such a dry coating process, it has the technical problem that equipment is expensive, a membrane formation rate is slow, and productivity is not high etc. On the other hand, the approach of using a metal alkoxide etc. as a start constituent, carrying out coating to a base material, and forming optical multilayers is learned, and the approach using alkoxides, such as Ti and Zr, as a high refractive-index ingredient is proposed. However, in these paint films, since an elevated temperature and long duration are needed for desiccation and a polymerization, a problem is in productivity. Moreover, although a certain amount of high refractive index can be obtained, since optical multilayers are used for the outermost layer, if physical reinforcement, such as a degree of hardness, and abrasion-proof nature, adhesion with a base material, is insufficient, and reinforcement is inadequate, it has the fault that practical use cannot be borne.

[0003] In order to improve these, the composite material of a metal alkoxide and an acrylic compound etc. is proposed as indicated by JP,8-297201,A.

[0004]

[Problem(s) to be Solved by the Invention] However, it is necessary to raise an acrylic monomer component ratio as these bipolar membrane constituents tend to raise physical reinforcement, such as a degree of hardness and abrasion-proof nature, and the volume ratio of the high refractive-index oxide which uses as a start constituent alkoxides, such

as Ti system which determines an optical property, is controlled, it has the fault that high refractive-index-ization cannot be achieved, and the constituent with which physical strength properties, such as a raise in a refractive index, a degree of hardness, abrasion-proof nature, and adhesion, are compatible is not found out.

[0005] Then, this invention has a high refractive index, and is excellent also in physical reinforcement, such as a degree of hardness, abrasion-proof nature, and adhesion, is cheap and aims at offering the coating constituent excellent in productivity.

[0006]

[Means for Solving the Problem] As a result of inquiring that an above-mentioned technical problem should be attained, it results in a header and this invention that a technical problem is solvable by forming the hybrid film of the isocyanate compound represented by denaturation objects, such as hexamethylene di-isocyanate (HDI), by using as a principal component the organic silicon compound which has a metal alkoxide and acryloyl radicals, such as Ti.

[0007] That is, invention according to claim 1 is the following general formula (1).

The metal alkoxide which can be expressed with  $M(OR)_n$  (an alkyl group and  $n$  are [  $M$  ] the metaled oxidation number for any one sort of metals of Ti, Ta, Zr, In, and Zn, and  $R$ ) and its hydrolyzate, and the following general formula (2)

$R'_x$  It is the coating constituent which uses as a principal component the organic silicon compound which can express with  $Si(OR)_y$  (the metaled oxidation number and  $x$  are the number of permutations of  $0 < x < y$  for the functional group and  $y$  to which an alkyl group and  $R'$  have the unsaturated bond in which polymerizations, such as a vinyl group, an acryloyl radical, and a methacryloyl radical, are possible at the end in  $R$ ), and its hydrolyzate.

[0008] Invention according to claim 2 is characterized by coming to contain the isocyanate compound which has at least two or more isocyanate radicals in a molecule further in said coating constituent in a high refractive-index coating constituent according to claim 1.

[0009] In a high refractive-index coating constituent according to claim 2, said ISON cyanate compound is the denaturation object of hexamethylene di-isocyanate (HDI), and invention according to claim 3 is characterized by average molecular weight being 500-3000.

[0010] In front claim 1 thru/or which a high refractive-index coating constituent given in three, as for invention according to claim 4,  $OH^{**}$  has 15-400 further in an account coating constituent, and average molecular weight is characterized by coming to contain the polyol resin of 3000-30000.

[0011] Invention according to claim 5 is characterized by coming to contain the high refraction ultrafine particle further chosen from crystalline titanium oxide of 1-50nm of mean diameters, a zirconium dioxide, a zinc oxide, and indium oxide into said coating constituent in which a high refractive-index coating constituent according to claim 1 to 4.

[0012] According to <operation> this invention, metal alkoxides, such as Ti, and the organic silicon compound of acryloyl radical content by considering as a principal component Generation of the oxide component which contributes to high refractive-index-ization by the hydrolysis product of the metal alkoxide of a general formula (1), A general formula (1) and the multiple oxide network of M-O-Si association by hydrolysis of the alkoxy group of the organometallic compound of (2) are generated. After coat formation by UV or carrying out EB exposure According to the can carry out things and according to heating polymerization and optical (EB) polymerization compound bridge formation bridge formation by the unsaturated bond radical in which polymerizations, such as an acryloyl radical in a coat, are possible is also made to generate since crosslinking density is made highly and is presenting uniform structure with the molecular level -- high refractive indexes, such as Ti, -- sufficient reinforcement can be demonstrated even if a degassed volume ratio is large. By adding further the isocyanate compound which has at least two or more isocyanate radicals in a molecule to the above-mentioned coating constituent The hybrid construction by generation of the urethane bond network by the reaction of the OH radical of the hydrolyzate of a coating constituent and the isocyanate radical of an isocyanate compound is formed, a degree of hardness is more high, and abrasion-proof nature is also good. The fault of the conventional coating agent can be improved sharply and a raise in a refractive index and a physical constituent compatible [ the improvement in on the strength ] are offered. Especially, by using an isocyanate compound as the TMP adduct object of HDI which reactivity with not an urethane prepolymer with big molecular weight but the water of a by-product, alcohol, etc. is low, and is low molecular weight etc., working life can be lengthened to some extent with constancy as a coating constituent, it is more homogeneous and the high hybrid film of crosslinking density can be formed. It can consider as the coating constituent which is excellent in improvement in coating nature, adhesion, and physical reinforcement etc. by furthermore adding the high polyol and a high raise in a refractive index of the above-mentioned hybrid film, compatibility, and reactivity, and the crystalline inorganic ultrafine particle which can carry out [ high intensity ]-izing.

[0013]

[Embodiment of the Invention] The gestalt of operation of this invention is explained to a detail.

[0014] after the coating constituent of this invention carries out coating of those with \*\* which consist of a coating constituent with which the isocyanate compound which has at least two or more isocyanate radicals in a molecule further is contained, and this to a base material, carries out stoving to it by using as a principal component the organic silicon compound which has a metal alkoxide and acryloyl radicals, such as Ti, and its hydrolyzate and forms a coat, it enables formation of a high refractive-index coat by performing the optical exposure of a UV etc.

[0015] Each component contained in a coating ingredient is explained in full detail below. Metal alkoxides used in this invention, such as Ti, are the following general formulas (1).

It can be expressed with  $M(OR)_n$  (for any one sort of Ti, Ta, Zr, In, and Zn, and R, an alkyl group and n are [ M ] a metaled oxidation number), and tetra--iso-propyl titanate, tetra--n-butyl titanate, tetra--n-butyl zirconate, etc. are illustrated. On the other hand, the organic silicon compound which has an acryloyl radical etc. is the following general formula (2).

R'<sub>x</sub> It can express with  $Si(OR)_y$  (for the functional group and y to which an alkyl group and R' have the unsaturated bond in which polymerizations, such as a vinyl group, an acryloyl radical, and a methacryloyl radical, are possible at the end in R, a metaled oxidation number and x are the number of permutations of  $0 < x < y$ ), and vinyltrimethoxysilane, acryloxypropyltrimethoxysilane, methacryloxy propyl trimethoxysilane, etc. are illustrated. Especially these organometallic compounds are suitable if it is not limited, it does not interfere at all even if it combines two or more sorts, and the metal alkoxide and the acryloyl radical content organic silicon compound are used together. Into a coating constituent, it is making organic-acid catalysts, such as p-toluenesulfonic acid, contain, and a hydrolysis reaction may be carried out to it being also at the moisture in atmospheric air after coating, and these organometallic compounds may carry out coat formation, and water (the catalyst of a hydrochloric acid etc. is included) can be added beforehand, and they can also use what carried out the hydrolysis reaction. In case water is added beforehand, it can use without [ special ] carrying out separation purification without the hydrolyzate of an organometallic compound being able to obtain a stable constituent by supposing that partial hydrolysis is carried out with the water of the amount of  $1/8 - 7/8$ , and leaving excessive water rather than the amount of water required for making all the alkoxyl groups of this organometallic compound hydrolyze. the above-mentioned adjustment controlling the

side reaction of an isocyanate compound and excessive water, or controlling the rate of hydrolysis of metallic compounds, controlling growth of a metallic-compounds polymer or raising compatibility with isocyanate -- it is -- phase separation -- controlling -- homogeneous -- molecule crosslinking density -- high -- the hybrid film of a molecular level -- \*\*\*\*\* -- it is -- it is \*\*.

[0016] Moreover, an isocyanate compound has two or more isocyanate radicals (NCO radical) in the molecule, and the prepolymer made to react in part with denaturation objects, such as an adduct object of G SOSHIA monomers, such as tolylene diisocyanate (it is described as Following TDI), xylylene diisocyanate (it is described as Following XDI), and hexamethylene di-isocyanate (it is described as Following HDI), and these monomers, a view let object, and a trimer, and a derivative, polyol, etc. can be used for it. As for the ability to form a homogeneous and transparent hybrid coat with high crosslinking density, the denaturation object of the low molecular weight of the molecular weight 500-3000 of the TMP adduct object of HDI, the view let object of HDI, a HDI trimer, etc. is suitable, without the hydrolyzate and compatibility of an organometallic compound being good and carrying out phase separation especially, at the time of coat formation. It is used as an urethane curing agent, and it is a thing, toxicity is also low used as a general-purpose article, and these denaturation objects are cheap.

[0017] By the system of the above-mentioned organometallic compound and an isocyanate compound, the crosslinking density of a coat can be too high, flexibility can be missing, or the polyol resin which the surface tuck just behind coating (adhesiveness) may remain, and has isocyanate and reactivity in consideration of the coating nature and stability of a paint film can be added. Although especially the polyol added into a coating constituent is not limited [ polyol / a polyester system, the Pori acrylic, / silicone denaturation acrylic ], it has OH \*\* 15-400, and its polyol of 3000-30000 is suitable for average molecular weight from cross-linking, coating nature, compatibility, etc.

[0018] Furthermore, by adding the high refraction ultrafine particle chosen from crystalline titanium oxide of 1-50nm of mean diameters, a zirconium dioxide, a zinc oxide, and indium oxide, abrasion-proof \*\*\*\*\* can be raised and a high refractive index can be formed further. Although the technique which adds these particles is well-known, a coat with the high adhesion of a better distributed condition, a filler, and a matrix is obtained, and effectiveness higher than the usual addition effectiveness is acquired rather than the combination with the hybrid system constituent of this invention has not a mere combination but the compatibility of the inorganic network of a coating constituent and the inorganic filler which are a matrix, and high compatibility and it

only distributes in organic resin.

[0019] If a radical polymerization initiator is added in case hardening by UV irradiation is performed, it is suitable, and it is benzoin ether system initiators, such as benzoin methyl ether, an acetophenone, and 2 and 1. - Although benzophenone system initiators, such as acetophenone system initiators, such as hydroxy cyclohexyl phenyl ketone, and a benzophenone, are mentioned, it is not limited especially. It can add to a coating constituent combining some of each components mentioned above, and can \*\* adding well-known additives, such as a dispersant, a stabilizing agent, a viscosity controlling agent, and a coloring agent, further in the range which does not spoil physical properties.

[0020] Well-known means, such as the dipping method and the roll coating method which are usually used, screen printing, and a spray method, are conventionally used for the method of application of a coating constituent. In accordance with the optical design of the purpose, selection adjustment of the thickness of a coat can be suitably carried out with the concentration and the amount of coating of liquid.

[0021] It is limited [ plastic film / neither / glass nor ], and especially the high refractive-index coating ingredient of this invention can carry out a laminating to various rebound ace court agents, a low refractive-index ingredient, and the ceramic vacuum evaporation film if needed further, and can also change and carry out the laminating of the presentation ratio of this invention.

[0022] A concrete example is given and the coating constituent of this invention is explained.

[0023]

[Example] By using as a base material the TAC film of 80-micrometer thickness which prepared the UV hardening resin HC layer (5 micrometers) in the front face, it combined and prepared and the acetophenone system initiator was added for the coating constituent 2% to the polymerization component as an initiator of creation and UV hardening so that it might become the rate which shows the ingredient of the following presentation in Table 1. Applied by the bar coating machine and carried out 100 degree-C-1min desiccation with the dryer, irradiate the ultraviolet rays of 1,000 mJ/cm<sup>2</sup> with a high pressure mercury vapor lamp, and it was made to harden, concentration adjustment was carried out suitably, the high refractive-index coat was formed so that optical thickness ( $nd = \text{refractive-index } n \times \text{thickness } d \text{ (nm)}$ ) might be set to  $nd=550 / 4nm$ , and the specimen for [ various ] a trial was obtained.

[0024] The specimen of the two-component system (example 2 of a comparison) of the system (example 1 of a comparison) and Ti alkoxide which do not contain a meta-chestnut ROKISHI silane as the specimen and the example of a comparison of

examples 1-3 of this invention, and 2 organic-functions acrylic compound was doubled and created. The compounding ratio of each component of the following coating constituent of each example and the example of a comparison was shown in Table 1.

[0025] The compound sol which carries out specified quantity mixing so that it may become the combination which shows (component A) tetra-isopropoxide titanate, and methacryloxy propyl trimethoxysilane in Table 1, mixed the ethyl-acetate mixed solvent (50/50wt%) with two mols of 0.1-N hydrochloric acids, and isopropyl alcohol to one mol of mixture, and carried out the stirring reaction at the room temperature for 2 hours.

[ <each / of a coating constituent / component> ] The ratio of each component made A1 as the titanium oxide component, and made A2 other component ratios.

(B) It is ethyl acetate about the TMP adduct object (commercial urethane curing agent) of HDI, and diluted solution.

(C) The solution of OH \*\* 130, average molecular weight 10000, and commercial acrylic polyol resin of Tg88 degree C. (Butyl acetate, ethyl-acetate partially aromatic solvent)

(D) Commercial urethane acrylic resin (two organic functions of average molecular weight 3000). Each solution carried out dilution adjustment of the solid content so that it might become 3wt(s)%.

[0026] The following evaluation approach estimated the specimen obtained above.

The reflection factor in 550nm was measured at 5 degrees of incident angles with the <evaluation trial> (1) optical-property spectrophotometer.

(2) The number of survival of a paint film estimated according to the cross-cut adherence test approach of adhesion coating General Test Procedures JIS-K5400.

(3) The abrasion of a paint film estimated according to the pencil scratch value test method of pencil degree-of-hardness coating General Test Procedures JIS-K5400.

(4) -proof -- by abrasion trial steel wool #0000, the appearance of the blemish according a five round trip abrasion trial to operation and viewing was inspected by the load of 250 g/cm2.

[0027]

[Table 1]

		実施例 1	実施例 2	実施例 3	比較例 1	比較例 2
配合比 (wt %)	A1	65	65	65	65	65
	A2	35	25	20	—	—
	B	—	10	10	20	—
	C	—	—	5	15	—
	D	—	—	—	—	35
反射率 (%)		13.3	12.9	13.2	13.0	12.8
密着性		100	98	100	100	100
鉛筆硬度		3H	3H	3H	H	2H
耐擦傷性		○	◎	○	×	△

A1：酸化シリコン成分  
 A2：メタクリレートモノマー成分  
 B：シリコン樹脂  
 C：アクリル樹脂  
 D：有機溶剤  
 耐擦傷性：◎傷なし、○かき傷あり、△かき傷つく、×著しく傷つく

[0028] As shown in Table 1, all had the reflection factor as high as about 13%, and were able to obtain the target (the refractive index of a coat was 1.8 about) high refractive-index layer. The coat using the coating constituent of this invention is excellent also in adhesion, a degree of hardness, and abrasion-proof nature. It turns out that each example of a comparison is inferior in a property in respect of reinforcement.

[0029]

[Effect of the Invention] As stated above, the coating constituent of this invention has compound metallic-oxide bridge formation of M-O-Si, and bridge formation and urethane bridge formation of an acrylic radical, can form the coat which presented the hybrid construction of the molecular level of a metallic oxide and an organic compound, and can form the coat which has the optical property and physical strength property of a high refractive index. That is, even if formed in the outermost layer of members, such as an antireflection film of a display, a harsh environment and the coat which can fully be equal also to handling can be formed, equipment cost is also comparatively cheap compared with vacuum evaporation etc., and the membrane formation (coating) rate of productivity is also high at 10 or more times, and easy to manufacture. Moreover, since the coat of the coating constituent of this invention is hardened by optical exposure etc. and the coating in low temperature is possible for it, it does so the effectiveness that it can mass-produce, that it is possible to roll round on a film etc. and to create by coating, and cheaply.

